ω,ω-PHENYLSULFONYLBROMOACETOPHENONE IN THE HANTZSCH CYCLIZATION

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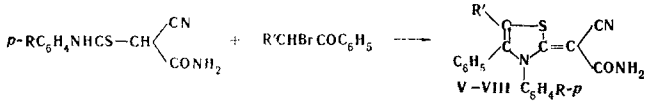
The preparation of a number of substituted 2-[(carbamoyl)cyanomethylene]-4,5-thiazolines is described.

Continuing our investigations of aromatic β-keto sulfones and their derivatives [1,3], we have found that thiazole derivatives containing an arylsulfonyl group in the 5-position can be obtained by the condensation of ω,ω-phenylsulfonylbromoacetophenone (I) with thioamides.

We obtained I by the bromination of ω-phenylsulfonylacetophenone with bromine in glacial acetic acid with heating. The bromine atom in I displays positive properties and undergoes quantitative iodometric titration. This property is apparently also responsible for the low reactivity of I in the cyclization with thioamides. Thus, when equimolecular amounts of I were refluxed in alcohol with compounds that usually react readily with α-halocarbonyl compounds (thioacetamide, thiourea, and diphenylthiourea), we obtained hard-to-separate resinous mixtures from which only unchanged I could be isolated in yields up to 70% (in the case of thioacetamide). The reaction proceeded in good yield only in the case of the phenylamide (II) and p-tolylamide (III) of carbamoylcyanothioacetic acid.

Thiazole derivatives with ω,ω-bromoacetophenone (IV) were obtained in alcohol from II-III for comparison. The reaction was complete in 30 min, as compared with 6-8 h in the case of I.



V R=H, R′=$C_6H_5SO_2$; VI R=CH_3, R′=$C_6H_5SO_2$; VII R=H, R′=H; VIII R=CH_3, R′=H

It is characteristic that the phenylamide and p-tolylamide of carbethoxycyanothioacetic acid do not react with I under these conditions, apparently because of steric hindrance, while they do react readily with IV [4].

The IR spectra of V-VI confirm their structure. There are bands at 3260-3270 (medium, NH), 2240 (strong, C≡N), 1120-1160 (strong) and 1350-1380 (strong, SO_2), and 1535-1670 and 1475-1510 cm^{-1} (strong, thiazoline ring) [5]. The IR spectra of VII-VIII are almost identical to the IR spectra of V-VI. Only bands characteristic for the SO_2 group are absent, and thiazoline ring bands appear in this region (1385-1445 cm^{-1}) [5].

EXPERIMENTAL

3,4-Diphenyl-5-phenylsulfonyl-2-[(carbamoyl)cyanomethylene]-4,5-thiazoline (V). This compound was obtained in 70% yield and had mp 219-220° (from alcohol). Found %: N 9.02; S 14.00. $C_{24}H_{17}N_3O_3S_2$. Calculated %: N 9.14; S 13.95.

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3-(p-Tolyl)-4-phenyl-5-phenylsulfonyl-2-[(carbamoyl)cyanomethylene]-4,5-thiazoline (VI). This compound was obtained in 63% yield and had mp 239-240° (from acetic acid). Found %: N 8.67; S 13.68. $C_{25}H_{19}N_3O_3S_2$. Calculated %: N 8.87; S 13.54.

3,4-Diphenyl-2-[(carbamoyl)cyanomethylene]-4,5-thiazoline (VII). This compound was obtained in 92% yield and had mp 272° (from alcohol). Found %: N 13.19. $C_{18}H_{13}N_3OS$. Calculated %: N 13.15.

3-(p-Tolyl)-4-phenyl-2-[(carbamoyl)cyanomethylene]-4,5-thiazoline (VIII). This compound was obtained in 90% yield and had mp 242° (from alcohol). Found %: N 12.61. $C_{19}H_{15}N_3OS$. Calculated %: N 12.60.

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